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Enhanced Adsorption of Methyl Orange by Vermiculite Modified by Cetyltrimethylammonium Bromide (CTMAB)

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Abstract

CTMAB-vermiculite, which can improve the vermiculite interlayer space and adsorption capacity of organic matter, has been obtained by using cetyltrimethylammonium bromide. The effects of the dosage of material, shaking time, the concentration of methyl orange, and the pH on the absorbent characteristics of methyl orange are studied by spectrophotoscopy. The structural characteristics of vermiculite and CTMAB-vermiculite have been studied through SEM. The results show that CTMAB-vermiculite changes dramatically -- its interlayer space becomes larger. The methyl orange removal rate of CTMAB-vermiculite is better than that of vermiculite. In about 30minutes. CTMAB-vermiculite can reach absorption equilibrium. Low pH conditions are conducive to CTMAB-vermiculite adsorption of methyl orange. The activated temperature should be controlled under the initial decomposition temperature of CTMAB, which can improve the reusability of recycled vermiculite.

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Keywords: Vermiculite; Cetyltrimethylammonium bromide; Methyl orange

1. Introduction

The worldwide production of dyes, especially for the textile industry, has increased in terms of volume, type, and complexity. In terms of world production, as much as 30% of dyes may be lost during the dyeing process, which can result in as much as 10 to 15% of unused dyestuff directly entering waterways.

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Dyestuff in water can adsorb and reflect light, thereby reducing the natural transparency of water, and can consume a lot of dissolved oxygen in water, causing water hypoxia and affecting aquatic life and microbial growth, and so in turn undermining the aquatic ecosystem [1].

Dye effluent normally contains about 10 to 50 mg/L, but even at 1 mg/L, dyes are easily noticeable and thus may be perceived as being contaminators, and unacceptable [2]. As a result, the treatment of dye effluent has been investigated extensively in modern times [3-5]. Adsorption is found to be the most efficient process for the treatment of effluents because of its ease of operation and the flexibility and simplicity of the design [6]; activated carbon adsorbent is used widely, however, due to high price, single adsorption ability, and complicated regeneration process [7] its use is limited. For this reason, exploring new and more efficient adsorption materials has important practical significance and wide application prospects for environmental restoration.

Vermiculite is usually derived by alteration or weathering from black mica, chlorite, illite and other minerals, as a secondary metamorphic mineral with magnesium, iron, aluminum and silicate. Vermiculite is a clay mineral with 2:1 crystalline structure [8], in each cell layer structure, the middle layer is an Al-O(OH) octahedral layer, the upper and lower layers being a silicon-oxygen tetrahedron layer [9]. Natural vermiculite has a lot of hydrophilic interlayer inorganic cations, the mineral surface usually surrounded by a thin layer of water film, which affects its adsorption properties, making it incapable of effectively removing pollutants, However, by ion exchanging, organic cations can be inserted into the interlayer of vermiculite, thus greatly reducing the hydrophilic phase of vermiculite; the interlayer space increases, the phase of hydrophobicity increases [10, 11]. This change significantly increases the adsorption ability of vermiculite for hydrophobic organic compounds, so organic vermiculite is an excellent form of adsorbent for organic pollutants [12-14].

In this paper, we use cetyltrimethylammonium bromide to modify natural vermiculite, thus creating a functional adsorption material, in order (i) acquire more information about the characteristics and the ability of CTMAB-vermiculite; and to (ii) study the possibilities of regeneration and reuse. The results of such studies can be of use in terms of screening new available fossil material for environmental restoration.

2. Materials and methods

2.1. Preparation of CTMAB- vermiculite

Put 50g of vermiculite into a beaker, add 500ml of distilled water so that the vermiculite becomes fully wet and dispersed in the water, then add the equivalent of 100% cation exchange capacity (CEC) of surfactant (cetyltrimethylammonium bromide). CEC is the cation exchange capacity of vermiculite. In measuring the CEC of vermiculite by the method of NH_4Cl-NH_4OAc [15], vermiculite CEC is found to be 18.071 cmol/kg of mineral. To achieve CTMAB-modified vermiculite: place the beaker in a water bath with a 60 ℃ constant temperature, stir for 2.0h, cool to room temperature, then perform filtration, repeatedly washing with distilled water 4 or 5 times, then dry at 80 ℃ , then activate at 105 ℃ for 2.0h, then sieve using 100 mesh.

Collect the used modified vermiculite, place in a drying oven at 80 ℃, then activate at 105, 150, 200, and500 ℃ each for 2h, then pass through 100-mesh sieve, and so derive recycled vermiculite.

2.2. Preparation of methyl orange solution

Methyl orange was purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd., China, and used without further purification. The methyl orange stock solution (1000mg/L) was prepared by dissolving an accurately weighed amount of methyl orange in distilled water. All working solutions of the desired concentrations were prepared by diluting the stock solution with distilled water. NaOH and HCl were purchased from the National Pharmaceutical Group Chemical Reagent Co., Ltd., China. All the chemicals used in this study were of analytical grade.

2.3. Analytical measurements

The structural characteristics of vermiculite and CTMAB-vermiculite have been studied through SEM (Hitachi S4800). The concentration of methyl orange was found by determining adsorbance at the characteristic wavelength using a 722N spectrophotometer. The aqueous solution's pH was measured by the Digisun Electronics System (Digital pH meter model 2001).

3. Results and discussion

3.1. Characterization of the adsorbent

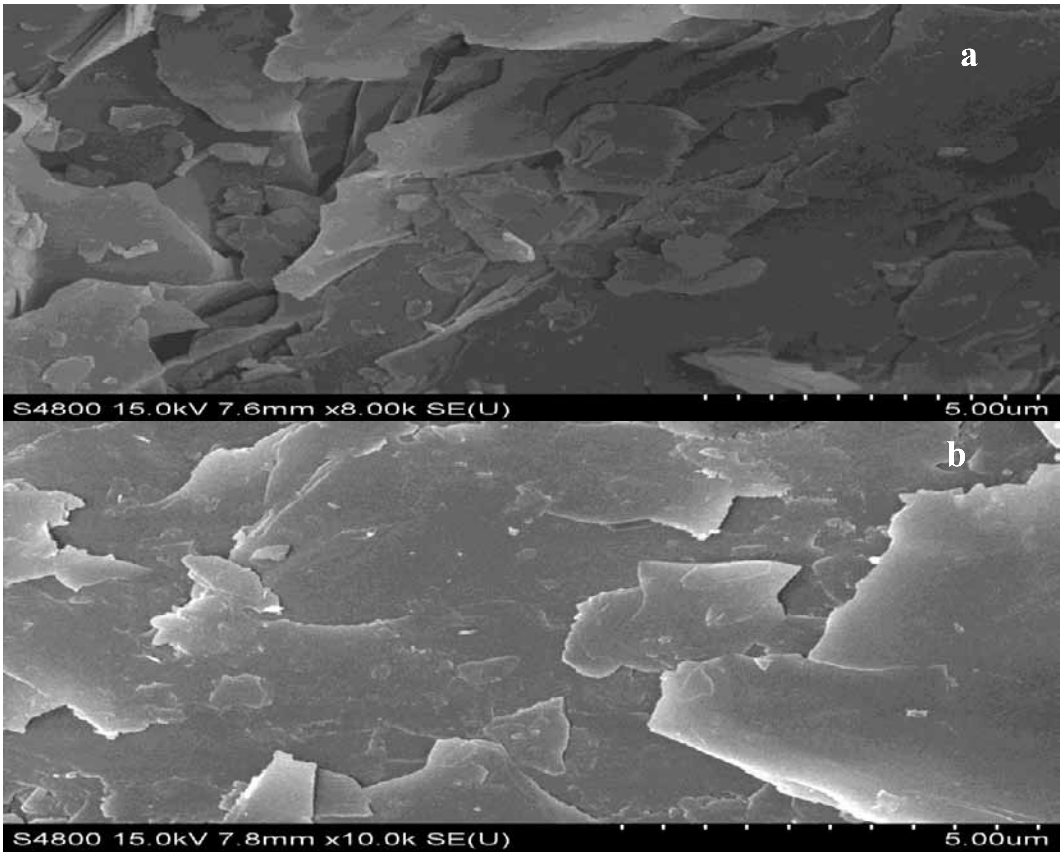

Fig.1. Micrographs of vermiculite and CTMAB-vermiculite (a: vermiculite; b: CTMAB-vermiculite).

The interlayer of vermiculite is a good place for a chemical reaction to occur, given the ability for interlayer exchange, interlayer adsorption, interlayer catalyst action, interlayer polymerization, and other processes [16, 17], but the original vermiculite interlayer has so many exchangeable cations, a large amount of water film is caused to form around the vermiculite, thus limiting the adsorption of organic pollutants. The mechanism of organically modified vermiculite allows organic surfactant to be inserted into the interlayer, stacked, and made into the hydrophobic organic phase formation in the interlayer [13, 18], so it is amenable to the adsorption of such organic pollutants as methyl orange, in that full advantage is taken of the enormous inner space of the vermiculite. Figure.1 shows micrographs of vermiculite and CTMAB-vermiculite structures. The interlayer of the CTMAB-vermiculite becomes larger and unlike the original compact vermiculite, due to CTMAB insertion into the layers [18].

3.2. Influence of adsorbent dosage

The effect of variation of the mass of adsorbent was studied by increasing the adsorbent dosage from 0.02g/20mL to 0.10g/20mL (Fig.2). The initial methyl orange concentration was 50mg/L. It was observed that, for vermiculite, and for CTMAB-vermiculite, the percent of adsorption varied from 1 to 3.3 and from 28.5 to 100, respectively. As can be seen, the percent of adsorption increased with the increase in adsorbent dosage. This can be attributed to the number of available adsorption sites increasing by an increase in adsorbent, resulting in an increase in methyl orange removal efficiency [19]. For a fixed initial methyl orange concentration, increasing the adsorbent dosage can provide a greater surface area or adsorption sites, so further experiments were carried out at a condition of 0.06g/20mL.

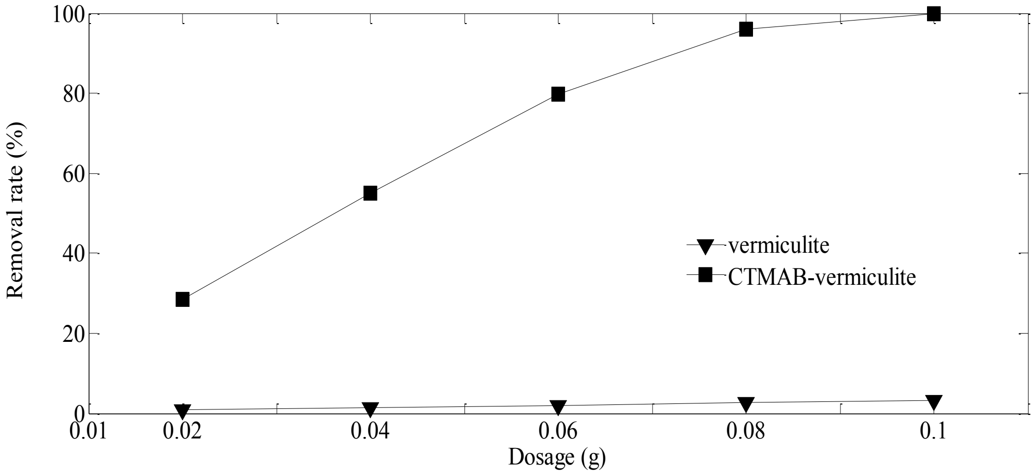

Fig.2. Effect of dosage on removal rate of methyl orange.

3.3. Influence of adsorption time

The influence of adsorption time was studied by varying the shaking time from 5 min to 75 min (Fig.3). The initial methyl orange concentration was 50mg/L. The result suggested that the percent of adsorption increased with the increase in shaking time. In about 30 min, the adsorbent can reach the adsorption equilibrium. On the other hand, as the shaking time increased, the adsorption capacity was not reduced, which indicates that the adsorption of methyl orange will not easily return to the solution; unlike with the adsorption of ions, with an increase in shaking time, boundary layer resistance is reduced and there is an increase in the mobility of ions in the solution [20]. It is inferred from this that the boundary layer resistance of methyl orange may be larger than that of ions. Further experiments were carried out at a shaking time of 30min.

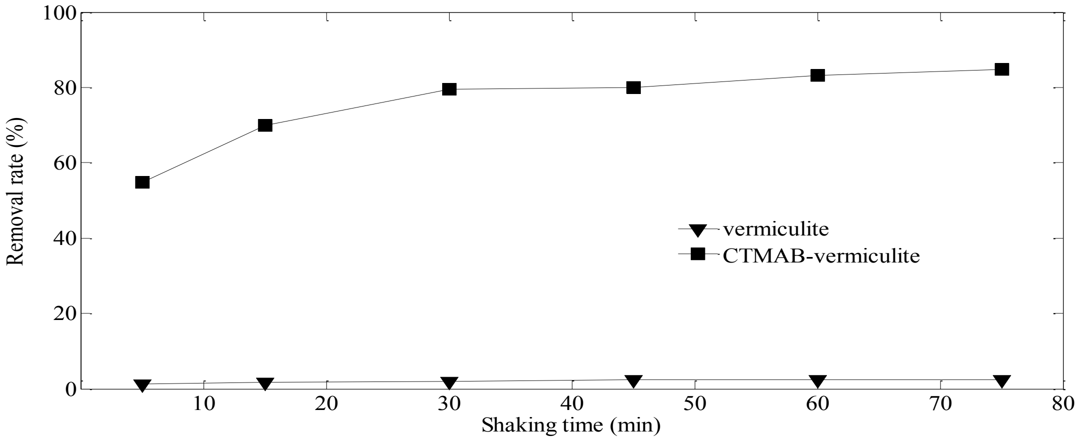

Fig.3. Effect of shaking time on removal rate of methyl orange.

3.4. *Effect of the initial concentration of methyl orange*

The effect of the initial methyl orange concentration was studied by varying the methyl orange concentrations from 20mg/L to 100mg/L (Fig.4). The results suggest that the percent of adsorption decreases with an increase in initial methyl orange concentration. This is mainly due to the total adsorption sites or the total adsorption capacity of certain amount of adsorbent is definite [19], and fewer pollutants, the total removal rate will be higher.

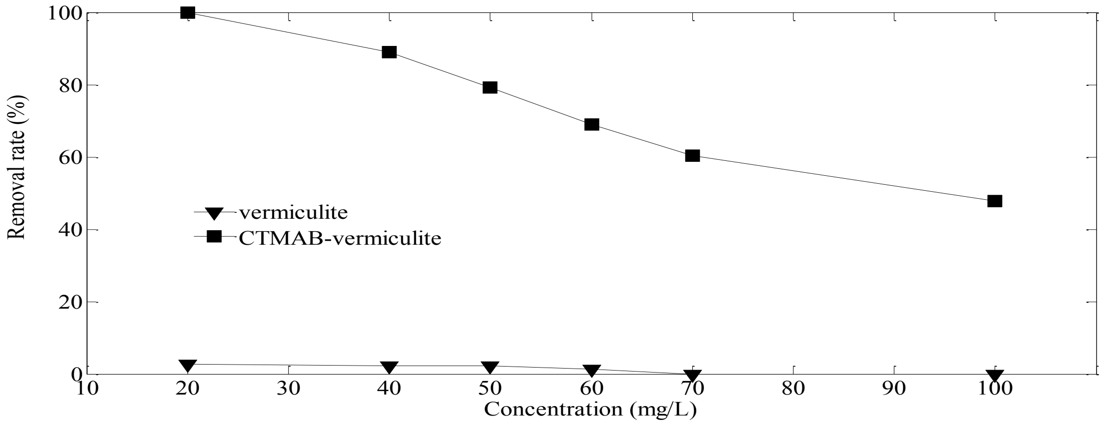

Fig.4. Effect of initial methyl orange concentration on removal rate of methyl orange.

3.5. Effect of the initial pH of the solution

The adsorption of methyl orange onto vermiculite and CTMAB-vermiculite was studied at different pH levels, varying from 3 to 11 (Fig.5), the initial methyl orange concentration being 50mg/L. Generally, the pH of the adsorption depends on the zero point charge of the methyl orange (pHzpc) and the charge of the adsorbent surface. The surface of the adsorbent will be positively charged at low pH and negatively charged at high pH [21]:

$—MOH+H^{+} = —MOH^{2+}$

$—MOH+H^{-} = —MO^{-}+H_{2}0$

Since methyl orange is an acid dye, its negative ions have an affinity for a positive charge of the adsorbent surface at lower pH, resulting in increased methyl orange adsorption. The result indicates that the pH of the methyl orange solution is a very important factor for the removal rate, can change the surface charge of CTMAB-vermiculite, and at the same time can change the molecular structure of methyl orange. The nature of adsorbent and pollutants can both have a greater influence on the adsorption [22].

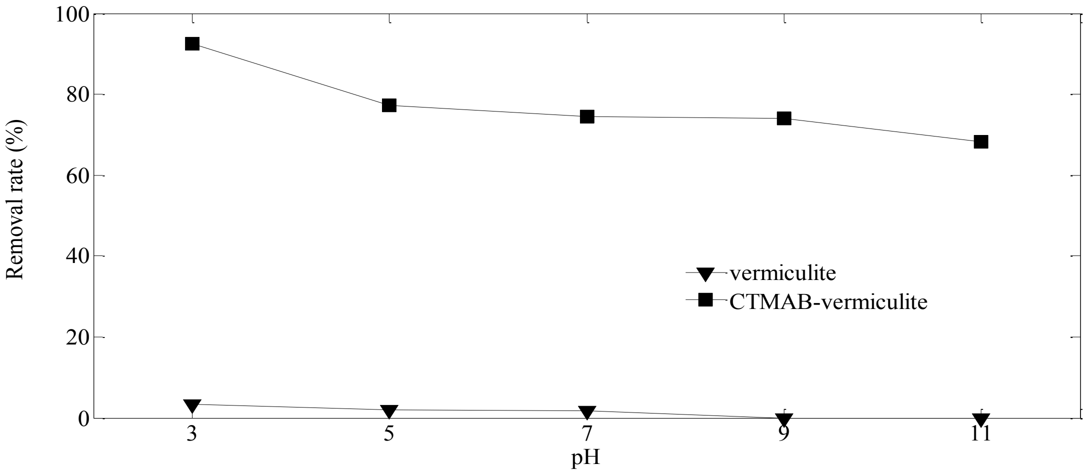

Fig.5. Effect of pH of solution on removal rate of methyl orange.

3.6. Effect of recycled CTMAB-vermiculite's activated temperature on removal rate of methyl orange

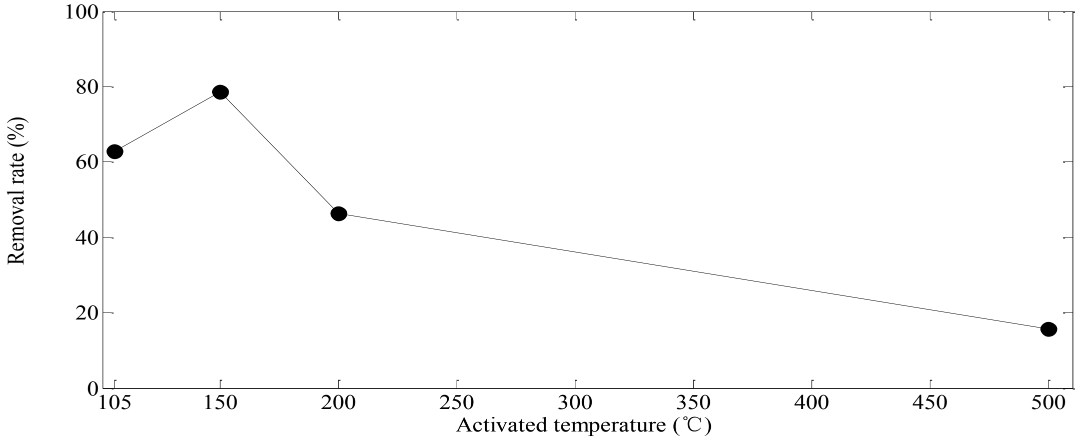

Fig.6. Effect of recycled CTMAB-vermiculite's activated temperature on removal rate of methyl orange.

The effect of recycled CTMAB-vermiculite's activated temperature on the removal rate of methyl orange is studied by adding 0.1g recycled vermiculite to a 20ml methyl orange solution, the initial concentration being 50mg/L, and then shocking for 30 min. The result is showed in Figure.6: when activated under 150 ℃, in the range of the test, the adsorption ability was the best. With an increase in temperature, the removal rate of methyl orange decreased. At less than 500 ℃, the removal rate of methyl orange decreased to 15.7%. It may be that in the process of organic pollutant adsorption, in the formation of a hydrophobic stacking arrangement of the organic phase between the vermiculite layers, the surfactant CTMAB plays a major role. While the surfactant CTMAB will start thermal decomposition at about 180 ℃, at temperatures higher than 250 ℃ the attached surfactant and methyl orange on the recycled CTMAB-vermiculite are completely decomposed, which results in a loss of adsorption [23] for the recycled vermiculite. Therefore, when reusing modified vermiculite, the activated temperature should be controlled at below the initial decomposition temperature of CTMAB.

4. Conclusion

The interlayer space of CTMAB-vermiculite increased and the adsorption ability of methyl orange solution was significantly improved. The percent of adsorption increased with an increase in the adsorbent dosage; when the initial concentration was increased, the percent of adsorption gradually decreased, and the adsorption of methyl orange into CTMAB-vermiculite was proved to be an efficient process, taking about 30 min to reach adsorption equilibrium. Low pH conditions were found to be conducive to the CTMAB-vermiculite adsorption of methyl orange. When reusing the modified vermiculite, the activated temperature should be controlled at below the initial decomposition temperature of CTMAB.

Acknowledgments

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